A STUDY OF THE QUANTITATIVE DETERMINATION OF TUNGSTEN.

DISSERTATION

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in
the Faculty of Pure Science,
Columbia University.

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LOUISE DURAND

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is due to Professor H. T. Beans who suggested this problem and under whose direction the work was consummated.

A STUDY OF THE QUANTITATIVE DETERMINATION OF TUNGSTEN.

The quantitative determination of tungsten is very important but at the same time very difficult. More and more commercial users are being found for this valuable metal on account of its adaptability in the electrical as well as the metallurgical field. The extended use of tungsten renders necessary its determination in many classes of materials, alloys and ores. Better analytical methods are needed to meet this increased demand.

The problems presented by a study of the behavior of tungsten are many and difficult of solution. Tungsten is most stable in the hexavalent state. As such it exists mainly as an anion, forming three tungstates; ortho, meta and para. Very little is as yet known about these tungstates; but it is possible that all three exist—probably in equilibrium. Tungstic acid is insoluble in acids except under special conditions. It forms soluble and insoluble complexes with ions of various elements such as silicon, boron, antimony, arsenic, phosphorus and vanadium. There are lower states of oxidation, notably the pentavalent and the quadrivalent. Definite compounds of lower valence exist as solids but form indefinite mixtures in an aqueous system. Most reducing agents lead to compounds of mixed valence. For this reason the hexavalent state is as yet the most important.

The use of various cations as precipitants has proved unsuccessful. Either the precipitation is incomplete, the precipitate of uncertain composition or the conditions for precipitation too limited to permit use in an ordinary analytical determination. In the absence of suitable inorganic reagents, organic salts have been tried and a fair degree of success has been attained with alkaloids. Various attempts have been

made to take advantage of the several valences to determine tungsten content by reduction methods, but thus far it has been impossible to find conditions for reduction to a definite state, so that this method is of no use for a quantitative estimation. Complex cations have been suggested as possible precipitants, but so far there has been little or no success along this line.

Barium, cadmium and mercury ions are among the cations which have been tried. Of these mercury has been most generally recommended. Pfordten[1], Defacqz[2], Watts[3], Desvergnes[4] and Berzelius[5] advocate its use in the determination of tungsten. A solution of $HgNO_3$ containing precipitated HgO in suspension is added to a neutral or faintly alkaline solution of tungstate. The precipitated Hg_2WO_4 is washed with a weak solution of $HgNO_3$, ignited and weighed as WO_3. Johnson[6] has objected to this method on the grounds that phosphorus, aluminum, vanadium and molybdenum precipitate under the same conditions and that it is practically impossible to wash the sodium salts from the Hg_2WO_4 when an alkaline fusion has been used for the solution of the ore. Moreover silicotungstic complexes form a mercury salt which is soluble in slightly acidulated warm water[7]. Complete precipitation is very seldom attained for these reasons. The use of other cations presents even greater difficulties.

Of the organic reagents the alkaloid, cinchonine, is the one generally recommended for the quantitative determination of tungsten. The one advantage over other alkaloids is its relative cheapness. Since all alkaloids are expensive this is an important item; especially in commercial work. An acid solution of tungstate is evaporated to dryness, taken up with water and the tungstate remaining in solution is precipitated by the addition of cinchonine hydrochloride. The cinchonine tungstate is washed with a dilute slightly acidulated solution of the reagent and ignited to WO_3. Molybdenum is the only element which precipitates under the same conditions. Vanadium, arsenic and phosphorus form complexes with tungstate which are precipitated with cinchonine tungstate. Of

these, phosphorus is the only one which presents serious difficulties. The distinct advantage of this method is that the precipitation of the tungstate is complete. Indeed, it is the only method thus far discovered which does give complete precipitation of tungstate.

Several reduction methods have been suggested. These methods all use a metal as a reducing agent; the metal usually being amalgamated and frequently used in a Jones' reductor. Variations in methods are largely concerned with the oxidation of the reduced tungstate. In some cases, the oxidation is carried out with permanganate, the permanganate acting directly on the reduced tungstate. In other cases an excess of ferric salt is used to oxidize the tungsten and followed by a titration of the reduced iron with permanganate. In still other cases an attempt is made to measure the amount of reduced tungstate by a direct titration with a ferric salt. None of these methods is in any measure successful.

Tungstate ion or complex tungstic acids are known to form complexes with several anions such as silicate, borate, arsenate, and phosphate. Though many of these compounds are mentioned in the literature, no attempt seems to have been made to utilize this property for the quantitative determination of tungsten. With this in mind, several complexes of this type were formed and some were found to yield difficultly soluble compounds. For example, a solution containing tungstate ion, boric acid and sodium pyrophosphate upon acidification with sulphuric acid gave a very finely divided white crystalline precipitate of unknown composition. Owing to the finely divided form in which it separated and the very narrow conditions under which tungstate was completely precipitated, this method was rejected as a possible analytical procedure. No other complexes of this type were found that seemed to offer a solution of the problem.

Precipitation reactions between tungstate ion and simple cations have been quite thoroughly investigated and have furnished no satisfactory quantitative method. The behavior of tungstate ion, however, with the complex cations of the cobalt

ammine series seems to have been practically overlooked. Reactions between tungstate ion and representatives of each type of cobalt ammine compound were tried qualitatively, and the chlorpentammine series was found to give the most promising results. While the quantitative investigation of these compounds was in progress, the unpublished thesis of Alsentzer[8] of the University of Pennsylvania came to our attention. Alsentzer was interested in the preparation of soluble, crystallizable compounds of cobalt, molybdenum and tungsten and prepared a number of such compounds. He was able to prepare soluble compounds of cobalt and tungsten which he found to be brom- and chlorpent-ammine cobalti tungstates. Alsentzer was further able to prepare soluble compounds of a more complex nature which contained tungsten in the cobalt complex. During the course of this work he mentioned some insoluble compounds of tungsten and chlorpentammine cobalti chloride; but since his investigation was concerned only with the preparation of soluble definitely crystalline compounds, he dismissed the insoluble compounds with the statement that they were of variable composition.

Of the chlorpentammines, chlorpentammine cobalti chloride was selected as the most satisfactory. It is easily prepared and fairly stable except in alkaline solution. When added to an acid solution of the tungstate a beautiful pink precipitate was formed. A small amount of tungstate remained in the solution. At first there seemed no way to overcome this difficulty. The conditions of precipitation were finally adjusted so that the filtrate gave no precipitate with cinchonine hydrochloride. The next problem was to determine the tungsten content of the complex. In his thesis Alsentzer had stated that his insoluble compounds were of variable composition. If this were true, the precipitate would have no analytical application unless there should prove to be a constant ratio between certain of its constituents. The complex contained both ammonia and water so that the possibility of drying to constant weight seemed impracticable. Therefore ignition was tried. The precipitate was first thoroughly washed with cold

water until all excess sodium, cobalti, and chloride ions were removed. It was then ignited in a muffle at 700°-900° C. The precipitate could be ignited to constant weight and, moreover, that weight could be reproduced. Evidently the compound was of definite composition; at least, after ignition. The ignited compounds were then analyzed for cobalt and tungsten. The cobalt-tungsten ratio was found to be 1 : 3.37.

PREPARATION OF SOLUTIONS AND MATERIALS.

Standard Tungstate Solution.

$Na_2WO_4 \cdot 2H_2O$ was recrystallized from distilled water and a solution made up to contain 6.0000 grams of this salt per liter solution. Its purity was tested by a determination of the WO_3 content according to the standard cinchonine method. To 50.15 cc. of tungstate solution containing 0.3009 grams of $Na_2WO_4 \cdot 2H_2O$ or 0.2115 grams of WO_3, 10 cc. of HCl (sp. gr. 1.18) was added and the solution evaporated to dryness. The residue was taken up with 200 cc. of hot water, acidified and allowed to simmer at the boiling point for half an hour. Six cubic centimeters of cinchonine hydrochloride was then added to the hot solution to precipitate the tungstate. After standing for twelve hours, the precipitate was filtered and washed first by decantation and later on the filter paper with cinchonine wash solution. The cinchonine tungstate was transferred to a weighed platinum crucible and ignited in a muffle at 900° C. The yellow residue was weighed and the WO_3 content thus determined was 0.2116 grams.

Standard Phosphate Solution.

KH_2PO_4 was made up so that one cubic centimeter of the phosphate solution was equivalent to one cubic centimeter of the standard tungstate solution. From the weight of KH_2PO_4 taken, 50 cc. of this solution contain 0.0653 grams of P_2O_5. The P_2O_5 content of this volume as determined by the magnesia mixture method was 0.0654 grams as shown in Table XIII.

Standard Sodium Hydroxide.

A tenth normal solution of NaOH free from CO_2 was prepared by diluting a saturated solution of NaOH with CO_2 free water. The standard of this solution in terms of P_2O_5 was determined by titrating the phosphomolybdate precipitate obtained from a definite volume of the standard KH_2PO_4. One cubic centimeter of the NaOH solution was equivalent to 0.000230 grams of P_2O_5.

Standard Potassium Permanganate.

A tenth normal solution of $KMnO_4$ was standardized against Bureau of Standards sodium oxalate in the usual way.

Magnesia Mixture.

This solution was made up according to the usual formula.

Ammonium Molybdate.

This solution was made and used according to the method of Beans and Johann[9].

I.—100 grams of ammonium molybdate was dissolved in 400 cc. of water, to which 80 cc. of NH_4OH (sp. gr. 0.90) had been added.

II.—400 cc. of HNO_3 (sp. gr. 1.42) was added to 600 cc. of water.

FOR USE—Pour one volume of I into two volumes of II.

Cinchonine Wash Solution.

30 cc. of the cinchonine reagent and 30 cc. of HCl (sp. gr. 1.18) were made up to one liter.

Cinchonine Hydrochloride Reagent.

The solution consisted of 100 grams of the alkaloid in one liter of 1 : 3 HCl (sp. gr. 1.18).

Chlorpentammine Cobalti Chloride Reagent.

The salt was prepared according to the method in Biltz[10] with a few modifications. The ammoniacal $CoCl_2$ was oxidized in the presence of excess NH_4Cl with $KMnO_4$ and the

MnO_2 filtered off. The solution was acidified with HCl and allowed to crystallize. The red chlorpentamine cobalti chloride was filtered from the mother liquor, washed with water and dried. The reagent used for the precipitation of tungstate ion was a saturated solution of this salt.

Precipitation of tungstate by chlorpentammine cobalti chloride proves a very simple and direct analytical method. To fifty cubic centimeters of the standard tungstate solution, twenty cubic centimeters of the chlorpentammine cobalti chloride reagent is added. Sometimes a precipitate is formed at this point; there is usually a slight turbidity. Five cubic centimeters of 6 M. HAc is then added to complete the precipitation of the tungstate. The precipitate is pink in color and coarsely divided so that it settles rather quickly. At the end of about four hours the supernatant liquid is a clear rose color and the precipitate is washed with cold water first by decantation and later on the filter paper until all excess of sodium, cobaltic and chloride ions is removed. The filter paper containing the precipitate is transferred to a weighed platinum crucible and ignited at 700°-900° C. to a light grayish blue color. The weight obtained from a definite amount of tungstate ion is constant, as is shown by the results given in Table I.

TABLE I.

Weight of Precipitates from 50 cc. of Standard Tungstate Solution.

0.2304 grams	0.2298 grams
0.2300	0.2297
0.2303	0.2302
0.2293	0.2302

The precision is 0.7×10^{-4}; practically the same as that of the cinchonine method.

As has been stated above, in order to determine the exact amount of tungstate by such a method, there must exist a constant ratio between two of the constituents. The ignited precipitates were consequently analyzed for cobalt and tungsten to determine the ratio between these ions in the complex. The precipitate was digested with sulphuric acid (sp. gr. 1.84), the cobalt going into solution as $CoSO_4$ while the WO_3, being in-

soluble in acids, remained unchanged. Ruegenberg and Smith[11] successfully used this method in a quantitative separation of MoO_3 and WO_3. The WO_3 was filtered off, washed with dilute acid and weighed. The filtrate and washings containing the cobalt were collected and evaporated to a small volume. The solution of $CoSO_4$ was then transferred to a weighed platinum crucible and heated until the excess H_2SO_4 was decomposed. The cobalt remained as the red crystalline $CoSO_4$ and was weighed as such.

As a check, the cobalt was also determined by the nitroso-beta-napthol method of Eder[12]. The conditions for precipitation given by Eder were not entirely satisfactory so that some alterations were necessary. About 0.1 grams of nitroso-beta-napthol in 10 cc. of acetic acid were used for every 0.01 grams of cobalt. The cobalt solution was neutralized, diluted to a volume of 200 cc. and the whole acidified by the addition of two drops of 12 M. HCl. The voluminous red precipitate was ignited and weighed as Co_3O_4.

TABLE II.

Co as $CoSO_4$

Weight Ignited Ppt.	Cobalt Content		Tungsten Content	Co/W in Ignited Ppt.
	25 cc. Standard Tungstate Solution			
grams	grams $CoSO_4$	grams CoO	grams WO_3	
0.1155	0.0206	0.0100	0.1051	3.397
0.1156	0.0207	0.0100	0.1057	3.417
0.1157	0.0207	0.0100	0.1057	3.417
0.1154	0.0209	0.0101	0.1054	3.373
	50 cc. Standard Tungsten Solution			
0.2305	0.0412	0.0200	0.2105	3.402
0.2305	0.0427	0.0207	0.2107	3.290
0.2305	0.0413	0.0200	0.2105	3.402
	Co as Co_3O_4			
	50 cc. Standard Tungsten Solution			
	grams Co_3O_4	grams CoO		
0.2303	0.0222	0.0207	0.2102	3.275
0.2303	0.0217	0.0203	0.2107	3.363
0.2306	0.0218	0.0203	0.2107	3.363

Table II shows that the ratio of cobalt to tungsten in the ignited precipitate is constant, having a value of $1 : 3.37 \pm 0.01$; even though the ratio of the two ions in the original solution was varied. Therefore, it was concluded that the chlorpentammine cobalti chloride precipitate of tungstate was a definite compound, and by calculation was found to contain 91.3% WO_3. The atomic weights used for all calculations were taken from the International Atomic Weight Table for 1925.

A method for the determination of tungsten has been described which is as accurate as the standard cinchonine method and at the same time is more rapid and free from many of its disadvantages. The reagent, chlorpentammine cobalti chloride, is easily prepared and very inexpensive. This method has the decided advantage over the cinchonine method that it does not require evaporation to dryness preliminary to precipitation. The precipitation is complete which is not true of any other except the cinchonine method. The excess of chlorpentammine cobalti chloride reagent in the filtrate causes very little trouble in any subsequent determinations whereas cinchonine interferes in practically every determination and must be destroyed before proceeding.

The cases in which chlorpentammine cobalti chloride as a precipitate for tungstate can not be used are comparatively few. A large amount of iron cannot be kept in solution at the hydrogen ion concentration necessary for the tungstate precipitation. Presence of phosphate is undesirable as it comes down with the tungstate, probably due to adsorption rather than to the formation of a complex as in the cinchonine method. Molybdate precipitates under the same conditions as tungstate in this method as well as in the cinchonine method. Otherwise the chlorpentammine cobalti chloride method is strongly advocated as a simple and direct method for the quantitative determination of tungsten. The comparatively short time necessary for a complete analysis is very much in its favor, particularly in commercial work.

In the various descriptions of methods in which cinchonine is used as the precipitant for tungstate no mention is made of

phosphorus as an interfering element. If phosphotungstic acid is added to a solution of an alkaloid, a heavy white precipitate of cinchonine phosphotungstate is formed. This reaction is often used as a test for the presence of alkaloids. When cinchonine hydrochloride is added to an acid solution containing phosphate and tungstate according to the cinchonine method for the determination of tungsten, a similar white precipitate is formed. The question naturally arises as to whether the precipitate formed in the tungsten determination with phosphorus present, is not cinchonine phosphotungstate; and if so, whether the ignited precipitate does not contain phosphorus as well as WO_3.

To test this hypothesis some determinations of tungsten by the cinchonine method were made in the presence of phosphorus. Fifty cubic centimeters of standard tungstate solution and 5 cc. of standard phosphate solution were precipitated by cinchonine and ignited at 900° C. in exactly the same way that the sodium tungstate solution had been standardized. A comparison of the two precipitates showed a marked difference in color. The pure WO_3 was the characteristic canary yellow while the other was a dull green. The green color of ignited tungsten trioxide is frequently noted in the literature and various explanations are advanced. Liempt [13] attributes the green color to a slight reduction brought about by alkali salts and claims sodium salts are most active, followed by those of lithium, rubidium and potassium. Smith and Lukens[14] support the statement of Liempt that the green color is due to sodium salts but omit reference to the apparently absurd reducing action of these salts invented by Liempt. In the present work a green color was never observed either in the presence or absence of sodium salts unless phosphate was present. Moreover as is shown in Table II these green precipitates weigh as much as 2½% more than pure WO_3 obtained under the same conditions except that phosphate was absent in the latter solutions. Furthermore, it will be shown in Table XIV that phosphorus may be recovered from these green precipitates.

TABLE III.

50 cc. Standard Tungstate Solution	50 cc. Standard Tungstate Solution + 50 cc. Standard Phosphate Solution 10 mole WO_3 to 1 mole P_2O_5
Ignited at 900° C.	
grams WO_3	Weight Ignited Ppt.
0.2115	0.2172
0.2122	0.2172
0.2115	0.2173
0.2112	0.2176
0.2117	0.2169
0.2103	0.2165
0.2116	0.2167
0.2119	0.2161
0.2114	0.2168
0.2117	0.2157
0.2119	0.2164
0.2120	0.2169
0.2120	0.2169
0.2121	0.2167
0.2113	0.2170
0.2114	0.2163
0.2120	0.2169
0.2119	0.2169
0.2115	0.2165
0.2110	0.2163
0.2112	0.2164
0.2117	0.2166
0.2117	0.2165
0.2119	0.2163
0.2115	0.2167
	0.2168
	0.2166
	0.2163
	0.2161
$0.2116 \pm 0.6 \times 10^{-4}$	$0.2167 \pm 0.6 \times 10^{-4}$

Matignon[15] and later Mellet[16] stated that high temperatures reduced WO_3 sometimes even to the metal and the carbide. A slight reduction of the yellow WO_3 might very well produce a green precipitate since the next lower oxide, W_2O_5, is a bright blue; but it must be remembered that such a green precipitate would weigh less than pure WO_3 on account of the

loss of oxygen. In order to be sure that the temperature has no effect, further determinations were made. For these determinations it was necessary to use another standard tungstate solution; hence the WO_3 content is slightly different. The precipitates were heated at 540°, 780°, and 900° C., and weighed to constant weight after each ignition. They were then subjected to treatment to oxidize any reduced tungstate, again heated to 900° C. and weighed. The loss in weight is within the precision of the measurement.

TABLE IV.

Temperature of Ignition.		
540° C.	780° C.	900° C.
grams WO_3	grams WO_3	grams WO_3
0.2143	0.2138	0.2136
0.2139	0.2134	0.2134
0.2145	0.2140	0.2140

From Table III it is quite evident that phosphorus interferes in the cinchonine method. In order to determine the extent of this interference, a series of experiments with equivalent amounts of tungstate and phosphate was run under the same conditions. It is interesting to note that the amount of phosphorus retained is not constant; that is, it does not increase in the same proportion as the ratio of phosphate to tungstate in the solution increases. This is shown by a comparison of Tables III and V.

TABLE V.

50 cc. Standard Tungstate Solution	50 cc. Standard Tungstate Solution + 50 cc. Standard Phosphate Solution 1 mole WO_3 to 1 mole P_2O_5 Ignited at 900° C.
grams WO_3	Weight Ignited Ppt.
	0.2178
	0.2179
	0.2178
	0.2180
0.2116 (Average from Table III)	0.2159
	0.2201
	0.2209
	0.2203

In order to show that this retention of phosphorus by WO_3 is perfectly general, a separation of WO_3 from a low phosphorus steel was carried out. For this purpose Bureau of Standards steel No. 50 was used and the Bureau of Standards method was followed. The final ignited precipitate which the method requires to be weighed as WO_3, had a distinct green color proving the presence of phosphorus. In this sample, however, since the WO_3—P_2O_5 ratio was 350 to 1, using the largest sample which is convenient in an analytical operation, it was found impossible to separate so small an amount of phosphorus even by the use of the correction method to be described later.

Because of the stability of the complex formed with tungstate and phosphate ions, and the fact that all the ions known to precipitate tungstate ion also, either precipitate phosphotungstates or yield tungstate precipitates which show a strong tendencey to adsorb phosphates; the separation of these ions by gravimetric methods seems impracticable. Many volumetric methods dependent upon the reduction and subsequent oxidation of tungsten have been proposed, but as will be shown later, none seems to possess even moderate accuracy. It was hoped, however, that since the problem involved in this work was largely concerned with the determination of tungsten in the presence of phosphorus, some advantage might follow from the use of the stable complex obtained by the addition of an excess of phosphate ion. None of the methods found in the literature employs this way of keeping tungsten in acid solution during the reduction process, and it would certainly hold out more promise than that of the tartrate and other organic complexes frequently advocated.

The choice of a reducing agent was an important matter. First of all, the products of reduction must not interfere and secondly, the excess of the reducing agent must be easily destroyed. These requirements eliminated such reagents as H_2S, Na_2SO_3, Na_2SeO_3 and $SnCl_2$. The choice of reducing agent was interdependent upon the method of reoxidizing the tungsten. The oxidizing agents commonly used are those which

can be made up as standard solutions. Preliminary experiments showed the reaction between tungstate and iodine to be slow and incomplete. Ferric ion proved wholly unsatisfactory since the end point is too indefinite to yield the proper precision. The use of dichromate usually necessitates an outside indicator which is extremely troublesome and lowers the precision. On the whole, $KMnO_4$ seemed the most promising oxidizing agent. This choice for oxidizing agent eliminates the possibility of an organic reducing agent, also the tungstate solution must be free from chloride ion. Consequently a metal and an acid seemed the simplest and best way to fulfil the conditions of this particular reduction. Cadmium, magnesium, zinc, lead, mercury and amalgams of zinc, cadmium and lead were tried with various acids. Unamalgamated zinc and H_2SO_4 was too rapid while other combinations were too slow to be practicable. A Jones' reductor prepared in the usual way proved most satisfactory.

At first the results were very discouraging, but by constant experimenting apparently successful conditions were found. To fifty cubic centimeters of the standard tungstate solution 10 grams of sodium pyrophosphate (which forms a complex with tungstate similar to that with orthophosphate) and 5cc. of H_2SO_4 (sp. gr. 1.84) were added. This solution was slowly poured through the reductor and collected in a flask. The reduction seemed to take place in two stages. In the upper part of the reductor a purple color appeared, gradually changing to a dark brown as the solution came in contact with more zinc, the brown color persisting throughout the remainder of the tube. The reduced solution was heated almost to boiling and titrated immediately with standard tenth normal potassium permanganate. The results were very consistent as shown in Table VI, and promised a very simple method for determining tungsten in the presence of phosphorus.

TABLE VI.

Cubic Centimeters 0.1092 N. $KMnO_4$	Valence Change
21.27	
21.28	
21.27	2.55
21.24	
21.26 (15 gms. $Na_4P_2O_7$)	

The tungstate obviously was not reduced to any one of the known states of oxidation, but rather to some combination of the known values. This would make no difference if under these conditions the reduction could always be carried to the same stage.

The next day four determinations were made in exactly the same way. The results checked among themselves but were somewhat lower than the first set.

TABLE VII.

Cubic Centimeters 0.1092 N. $KMnO_4$	Valence Change
20.85	
20.85	2.50
20.80	
20.85	

Evidently some condition had not been carefully enough controlled. Consequently the temperature at which the reduced solutions were titrated was regulated to $75° \pm 1°$ and the experiment repeated, all other conditions being maintained as in the two previous runs.

TABLE VIII.

Cubic Centimeters 0.1092 N. $KMnO_4$	Valence Change
20.60	
20.54	2.47
20.38	
20.38	

The temperature of the titration did not seem to be the controlling factor, for the results did not even agree among themselves as they had previously.

About this time a dark color was noticed throughout the Jones' reductor. It seemed to be some sort of a deposit on the amalgamated zinc. Since the tungstate was reduced to a brown color by the action in the reductor, this deposit was thought to be some of the reduced tungstate. The column was first replaced by new zinc but the results were even more erratic and the dark coating soon reappeared. Thinking that this deposit might be the cause of the erratic reduction values obtained, a method of correcting for it was sought. A dilute solution of ammonia poured through the reductor seemed to restore the bright surface to the amalgamated zinc. If the deposit were reduced tungstate, and if the action of the ammonia dissolved it from the surface of the zinc, a correction might be made by titrating any tungsten contained in the ammoniacal solution. This procedure was followed but, judging from the results in Table IX, was not successful.

TABLE IX.

Cubic Centimeters 0.1005 N. $KMnO_4$	Valence Change
22.13	2.45
22.01	2.44
23.02	2.55
23.03	2.55

Other vain attempts were made to locate the trouble. The temperature of the titration was regulated by 5° intervals from 20° to 85° C. The temperature of the solution before reduction was raised as high as was practicable. A pad of glass wool was put on the top of the zinc column to prevent reduction before the tungstate solution came into actual contact with the main column of zinc. A small amount of unamalgamated zinc was added to the tungstate to start the reduction before the solution was poured through the reductor. Zinc was again added after the reduction to insure complete reaction. The hydrogen ion concentration was varied. The reduced tungstate was immediately passed into a ferric solution in order to prevent oxidation by the air before titration. The pyrophosphate was replaced by other ions known to form

soluble complexes with tungstate ion. Of these a solution containing 50 grams of boric acid and 50 grams of sodium pyrophosphate to the liter was most successful. Fifty cubic centimeters of this solution and 5 cc. of H_2SO_4 (sp. gr. 1.84) were added to 50 cc. of the standard tungstate solution and run through the reductor. Table X shows the result of these determinations. As before the runs agreed among themselves but did not check the runs in any other set.

TABLE X.

Cubic Centimeters 0.1005 N. $KMnO_4$	Valence Change
22.09	2.44
23.20	2.56
23.23	2.56
22.80	2.52
22.92	2.53
22.44	2.48
22.18	2.45
21.96	2.42

Knecht and Hibbert [17] claims that they are able to get quantitative reduction to WO_2 with zinc and HCl. They add 70-80 cc. of HCl (27%) and 14-15 grams of zinc to a warm solution of tungstate and allow the reduction to continue until a red color appears. Carbon dioxide is then passed through the solution and the whole titrated with standard ferric alum solution using KCNS as indicator. There are several objections to this method as a quantitative procedure. First, there is no possible way of regulating the reduction except by the hydrogen ion concentration; secondly, the use of KCNS as an indicator is anything but accurate. However, this method was tried in the hope that it would throw some light on the problem. At no time was a red color observed although the reaction was continued until the zinc was completely oxidized. Table XI shows the results of these determinations. The runs do not check each other nor was the tungstate completely reduced to WO_2.

TABLE XI.

Cubic Centimeters 0.1005 N. $KMnO_4$	Valence Change
21.67	1.90
21.00	1.84
21.25	1.86

Freih[18] reduces as above to WO_2. When the reduction is complete as denoted by the appearance of a red color, the solution is cooled and an excess of $KMnO_4$, $MnSO_4$ and H_2SO_4 added. An excess of standard ferrous sulphate solution is introduced, and the excess titrated with standard permanganate. The use of $MnSO_4$ or "preventive" solution is generally avoided in analytical work but Freih claims very good results. Table XII shows the result of reduction carried on by this method. At no time did a red color appear even though the reduction went beyond WO_2.

TABLE XII.

Cubic Centimeters 0.1006 N. $KMnO_4$	Cubic Centimeters 0.0987 N. $FeSO_4$	Valence Change
29.60	9.82	2.18
30.06	9.82	2.23

Kuklin[19] carried out the reduction with zinc and HCl titrating with standard $KMnO_4$. His method was even less satisfactory.

Someya[20, 21] published a reduction method for the determination of tungsten using HCl and liquid amalgams of bismuth, lead, zinc or cadmium. The reduction is carried on in a large separatory funnel in an atmosphere of carbon dioxide. A tungstate solution is shaken with the liquid amalgam at 50° C. until the "intensity of the color increases no more." It must be borne in mind that it is quite impossible to follow these directions since changes in color of deeply colored solutions are not discernible. "The titration is made with $KMnO_4$ in the presence of 5 cc. of concentrated $MnSO_4$, taking perfect colorlessness as the end point." He claims that the bismuth amalgam reduces the tungstate quantitatively to the pentavalent state while the other amalgams carry the reduction to the

tervalent state. Considering the method, Someya's results are phenomenal. Except in the case of zinc where the violence of the reaction caused him some trouble, he claims an error of not more than one part in a thousand. Unfortunately his results could not be duplicated. It was impossible to prevent some of the reduced tungstate from adhering to the amalgam. The quantity of $PbCl_2$ formed in the case of the lead amalgam did not interfere during the reduction which was carried on in a concentrated HCl solution, but gave serious trouble when it came to the titration. Many permanganate titrations carried out in a solution of high chloride ion concentration are rendered possible by adding large concentrations of $MnSO_4$. The use of $MnSO_4$ in this titration, however, does not seem to be based on very sound theoretical reasoning, and the results certainly condemn its practicability.

Since Someya seems to think that there is some advantage in carrying out the reduction of tungstate in a hydrochloric acid solution, and since the titration of such a solution by permanganate is at least a questionable procedure, it was decided to substitute the dichromate titration described by Knop[22]. In this method diphenylamine is used as an inside indicator and the color change is from the green of the chromic ion, through a grayish blue to an intense violet-blue coloration caused by the addition of one drop which on the further addition of dichromate remains unchanged. While this method may be satisfactory for an iron determination, and in fact a concordant series of results was obtained in titrating a standard ferrous solution; still no conditions could be found under which the method could be used for a tungsten determination. In order to eliminate any error due to the reaction in the reductor, aliquot parts of a reduced tungstate solution were used for these tests. The reaction was very slow and the end point quite indefinite.

The results of these experiments show that there are at least two reasons for the inability to determine tungsten by reduction methods. In the first place, there seems to be no reducing agent, at least under the conditions so far discovered,

which will reduce all the tungstate to a definite valence state. In the second place, all those methods which employ an amalgamated metal as the reducing agent result in partial deposition of the tungsten on the amalgamated metal:—probably in the form of one of the lower oxides.

All attempts to devise a simple and direct method for the determination of tungstate in the presence of phosphates having failed, the standard cinchonine method for the determination of tungsten was investigated in respect to the possibility of correcting the WO_3 residue for the P_2O_5 which it invariably contains. Hinrickson[23] had proposed a method which proved unsatisfactory and indeed was contrary to his own careful analysis of the requirements of such a method. Essentially Hinrickson converts the ignited WO_3 containing P_2O_5 into soluble tungstate and phosphate by fusion with sodium carbonate. After acidification he precipitates the phosphate from this solution with ammonium molybdate reagent. In view of his statements in his introduction of this method to the effect that tungstate will always precipitate with phosphomolybdate and that the addition of tartrate, tannate, etc., to keep tungstate in solution interferes with the precipitation of phosphomolybdate, his method is quite impossible.

Later Mellet[16] attacked the same problem. Without going into the details of this method, its status as a precise analytical procedure may be set forth by the following translation of the author's comment upon it. "Due to a very slight solubility of the quinoline salt (here used as a precipitant for tungsten) the weight of the anhydrous phosphotungstate is a little low, but since the determination of the phosphate contained in this residue also gives a result a little low in P_2O_5, the weight of WO_3 obtained by difference is generally the same as, or slightly higher than the theoretical figure."

Having in mind the unsuccessful attempts made by others the following procedure was adopted. To the solution containing phosphate and tungstate made slightly alkaline with ammonium hydroxide, magnesia mixture was added in slight excess and the precipitate of $MgNH_4PO_4$ allowed to stand for

twelve hours. The $MgNH_4PO_4$ was then filtered onto a weighed porous bottom crucible, washed with dilute ammonia containing NH_4NO_3 and then ignited to magnesium pyrophosphate. The tungsten in the filtrate was precipitated by cinchonine as described above. This procedure gives a quantitative method for the separation of phosphate from tungstate as shown by the following table of results.

TABLE XIII.

Weight $Mg_2P_2O_7$ from 50 cc. of Standard Phosphate Solution	Weight WO_3 from 50 cc. of Standard Tungstate Solution	Wgt. $Mg_2P_2O_7$ from 50 cc. of Standard Phosphate Solution	Wgt. WO_3 from 50 cc. of Standard Phosphate Solution
		50 cc. of Standard Tungstate Solution	50 cc. of Standard Tungstate Solution
0.1025 grs.	0.2110 grs.	0.1026 grs.	0.2113 grs.
0.1026	0.2112	0.1025	0.2113
0.1025	0.2113	0.1026	0.2114

Finally, to show the practical application of this method to an analytical procedure a solution containing 0.0065 grs. of P_2O_5 and 0.2115 grs. of WO_3 was prepared. The tungstate and part of the phosphate were precipitated by cinchonine as previously described. The precipitate was ignited and weighed. The ignited precipitates were green in color and weighed more than the total WO_3 content as shown in the first column of Table XIV. These green precipitates were fused with Na_2CO_3. After cooling the melt was dissolved in water and filtered if necessary. The solution was then made slightly acid with HCl and boiled to expel the CO_2. Any separation of tungstic acid at this point may be disregarded as it will redissolve in the next operation. The solution was made alkaline with ammonium hydroxide and allowed to cool. Magnesia mixture was then added and the solution allowed to stand for twelve hours to precipitate the phosphate. The $MgNH_4PO_4$ was then filtered and washed with NH_4OH-NH_4NO_3 wash solution. The filtrate was reserved for the tungsten determination. The precipitate of $MgNH_4PO_4$ was dissolved in 6 N. HNO_3 and the phosphate in this solution determined by the ammonium molybdate method as described by Beans and Johann[9]. These results are shown in the second

column of Table XIV. The filtrate from the magnesia mixture precipitate was acidified with HCl and the tungstate, now free from phosphate, again precipitated by cinchonine, ignited and weighed as WO_3. These ignited precipitates were always pure yellow. The results are given in the last column of Table XIV. To the solution which was obtained from the original cinchonine precipitate magnesium salts in excess of the phosphate were added and the solution evaporated to dryness. The dry residue was then ignited to destroy all organic matter. The residue was dissolved in dilute nitric acid and the phosphate was determined by the molybdate method as before. The results are given in the third column of Table XIV. The total phosphorus is obtained from these two phosphorus determinations and is given in the fourth column of Table XIV.

TABLE XIV.

Solution containing 0.0065 grs. P_2O_5 and 0.2115 grs. WO_3

Ignited Cinchonine Precipitate grams	P in Cinchonine Precipitate grams P_2O_5	P in Solution grams P_2O_5	Total P grams P_2O_5	W in Cinchonine Precipitate grams WO_3
0.2170	0.0032	0.0036	0.0068	0.2110
0.2169	0.0040	0.0029	0.0069	0.2105
0.2161	0.0033	0.0039	0.0072	0.2109

As is shown by Table XIV, the results given by this method are entirely satisfactory. The method, however, requires considerable time and a simpler and more direct method for the determination of tungsten in the presence of phosphorus is greatly needed.

SUMMARY.

1. A new reagent for the precipitation of tungsten has been discovered and the conditions for its application to a quantitative determination of tungsten have been described.

2. Various methods for the determination of tungsten have been discussed in relation to the respective limitations.

3. Proof of inclusion of phosphorus in the tungsten trioxid obtained in the standard cinchonine method for the determination of tungsten has been established. It has also been established that the peculiar green color of tungsten trioxid precipitates frequently mentioned in the literature is due to the presence of phosphorus.

4. Definite proof has been given that in those reduction methods in which an amalgamated metal is used as the reducing agent some tungsten is always withdrawn from the solution and left as a deposit on the metal. No method of preventing this was found.

5. A quantitative determination of tungsten and phosphorus in the presence of each other has been worked out. While satisfactory as to results, it is complicated and time-consuming. Need of a more direct method is indicated.

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